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ORE MINERALOGY AND GEOCHEMISTRY RELATIONSHIPS IN BĂIȚA BIHOR ORE DEPOSIT, APUSENI MOUNTAINS, ROMANIA - BLIDAR CONTACT CASE STUDY

Mădălina Paula ANDRII*, Călin Gabriel TĂMAȘ**

Department of Geology, Faculty of Biology and Geology, Babeș-Bolyai University, 1, M. Kogălniceanu Str., 400084 Cluj-Napoca, Romania; e-mail: **andrii.madalina@hotmail.com*, ***calin.tamas@ubbcluj.ro*

Abstract: With a complex ore mineralogy, Băița Bihor ore deposit, North Apuseni Mountains, Romania represents a classic example of distal skarn related ore deposit from the northern extremity of the Banatitic Magmatic and Metallogenetic Belt. An important control factor for the ore genesis is a tectonic structure (thrust-fault) known as Blidar Contact. The geochemical analysis of the ore from Blidar Contact pointed out among others high Cu grade (22.8 wt %), and significant precious metals grades (0.91 ppm Au and > 500 ppm Ag). The W and Sn grades (530 and 110 ppm respectively) suggest the presence of scheelite and of a Sn-bearing mineral within the analyzed ore.

Key words: geochemistry, skarn, Băița Bihor, Apuseni Mountains.

Introduction

Located in the north-western part of the Apuseni Mountains, Băița Bihor represents the most significant ore deposit from the northern extremity of the Banatitic Magmatic and Metallogenetic Belt - BMMB (Berza et al., 1998). This ore deposit is known for its high-grade ores and its complex mineralogy, with over 120 minerals described so far (Udubașa, 2003). Among these minerals, several have been identified for the first time from Băița Bihor ore deposit, *e.g.* cuproneyite (Ilinca et al, 2010), grațianite (Ciobanu et al., 2014), makovickyite (Žák et al., 1994), and paděraite (Mumme and Žák, 1985).

The Băița Bihor is a Cu-dominated polymetallic ore deposit and represents a classic example of distal skarn related ores (Vlad, 1993). It also illustrates the outstanding metallogenetic role of the regional and local structural control (Stoici, 1974).

Despite the scientific and the economic potential of Băița Bihor ore deposit only few geochemical studies have been carried out in the last decades, and thus the reference work still remains Stoici (1983). The present contribution offers additional data for Băița Bihor ore deposit from geochemical and mineralogical perspectives regarding the so-called Blidar Contact, an important tectonic structure that favored the ore deposition (Cioflica et al., 1977; Stoici, 1974).

The access to the underground mining works and to the ore body related to Blidar contact is presently limited; therefore, the sampling was not possible. However, for the present study, we used old ore collection samples and this fact highlights the importance of ore/mineral collections for the today's science.

Geological Setting

Băița-Bihor ore deposit is part of the Banatitic Magmatic and Metallogenetic Belt (BMMB), and its genesis is closely related to the overall geologic evolution of the belt. Over the time, the genesis of the BMMB was extremely disputed and several models have been proposed (*e.g.*, Gallhofer et al., 2015; Zimmerman et al., 2008, etc.). The most recent model stated by Gallhofer et al. (2015) suggests that the magmatic activity within the belt started during Austrian tectogenesis and was triggered by the north-dipping subduction of Neotethys (a Vardar ocean branch) with a magmatic ascension controlled by the steepening (roll-back) of the subducting slab.

The BMMB was divided based on major tectonic structures in five distinct sections (Gallhofer et al., 2015): Apuseni, Banat, Timok, Panagyurishte and Eastern Srednogorie (Fig. 1a). The onset and the end of the Banatitic magmatism within the Apuseni section of the BMMB that includes the Băița Bihor ore deposit, was determined by Cioflica et al. (1995), who suggested the time interval 91±4 to 43±2 Ma. More recently, Zimmerman et al. (2008) places the onset of the Banatitic magmatism for Apuseni Mountains (Băița Bihor skarns) at 80.6 Ma and the end at 78.7 Ma. The time span of the magmatic activity was more recently constrained by Gallhofer et al. (2015) at ~80.8-75.5 Ma.

The magmatic products hosted within the belt are known as "banatites" (according to von Cotta's term), and are generally calc-alkaline with a wide range of petrographic varieties *i.e.* diorite, andesite, granite, dacite, rhyolite, granodiorite (Berza et al., 1988; Heinrich and Neubauer, 2002; Vlad and Berza, 2003; Gallhofer et al., 2015; etc). However, Gallhofer et al. (2015) highlights the presence within the Apuseni section of the Banatitic belt, of high-K calc-alkaline rocks, with a dominant dacite-rhyolite petrographical range. Berza et al. (1998) mentioned for the North Apuseni, the presence of acid volcanism accompanied by granodiorite-granite pluton.

Beside the productive high-K calc-alkaline magmatism materialized through a deep-seated granite to granodiorite-diorite batholith accompanied by several dykes with a composition ranging from basic to intermediate (Stoicovici and Selegean, 1970), the structural control was the main factor that contributed to the genesis of the ores from Băița Bihor. The regional and local structural setting with thrust planes (*i.e.* Blidar Contact), fractures and faults intersections controlled the upwelling of the mineralizing fluids within the Băița Bihor perimeter. The dominant carbonatic rocks of the nappe system represented another control (lithological) that allowed the distal skarn and related polymetallic ore bodies formation.

Local Geology

The geological structure of the Băița-Bihor area is composed of a nappe system formed mainly during pre-Gossau tectogenesis (Fig. 1b). In lower position are located Jurassic-Lower Cretaceous detritic and calcareous formations that belong to the Bihor Unit, which is thrusted along the Blidar Contact by Triassic sedimentary rocks (limestones, dolomites and sandstones) of the Codru Unit (Stoici, 1983). These sedimentary units are covered by the Arieșeni nappe, which is composed of Permian (early Carboniferous?)-Lower Triassic detritic series (Stoici, 1983).

The Laramian (Upper Cretaceous) magmatism from Băița-Bihor area triggered thermal and metasomatic changes within the sedimentary rock pile and led to the development around the magmatic body of an aureole of contact metamorphism developed up to 1.5 km distance away of the batholith (Cioflica et al., 1974). Hornfels, calcic marbles and several types of skarns (*i.e.* calcic, magnesium, and calco-magnesium) and associated ore bodies were formed closely dependent on the structural peculiarities of the perimeter. One of the most important tectonic structure that facilitated the ore deposition is represented by the so-called Blidar Contact (thrust-fault) that follows a NW-SE direction and has a dip of 45-50º SW (Cioflica et al., 1971). The ore body along Blidar Contact has a tabular morphology measuring over 600 m in length and 5-15 m in width (Cioflica et al, 1971). Furthermore, the ore deposited on Blidar contact has a west to east lateral zonation, *i.e. i*) Mo (-Bi, Cu, W) deep-proximal zone; *ii*) Cu (-Bi, W) median zone, and *iii*) Pb-Zn distal zone (Stoici, 1974).

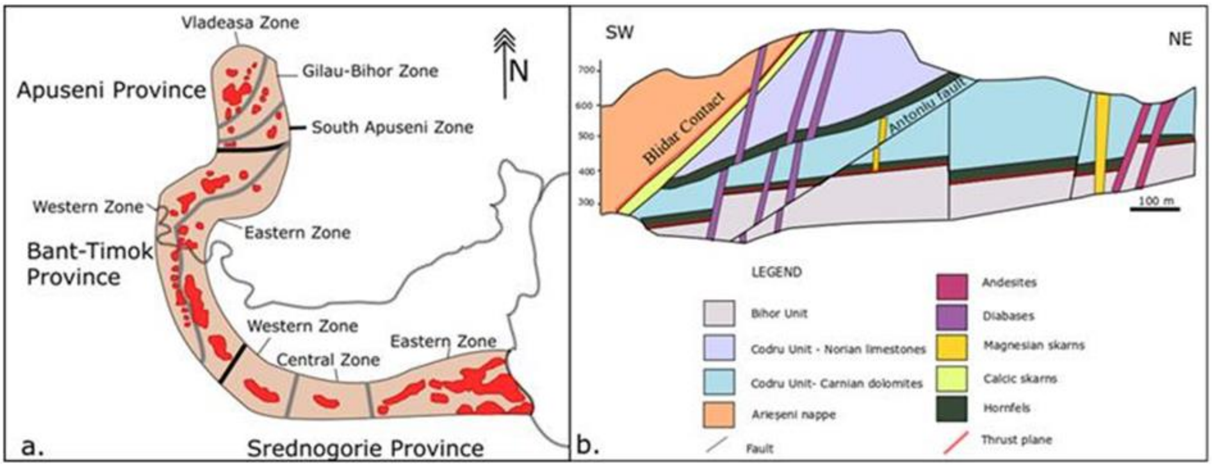

Fig. 1. Regional and local geological setting: a) simplified delineation of the Banatitic Magmatic and Metallogenetic Belt (BMMB) sections (Vlad, 2011; adapted after Vlad and Berza, 2003); b) simplified geological cross-section through Băița Bihor ore deposit (Stoici, 1974).

Materials and methods

Due to the unsafe passage through the underground mining works that give access to the Blidar Contact ore body, the studied material consists of several ore samples collected by Professor Ioan Mârza in 1971 and presently preserved in "Valeriu Lucca" Ore Deposit Collection, Department of Geology, Babeş-Bolyai University, Cluj-Napoca.

The macroscopic observations allowed to select a representative sample for the bulk composition of the ore. The sample dimensions are 23x16 cm and it is bornite rich. A slice from this sample (Fig. 2) was selected for multi-elemental geochemical analyses.

Fig. 2. Slice of the ore sample from Blidar Contact ore body used for geochemical analyses. Bornite (dark purple) is the main ore mineral and is associated to wollastonite (white).

The multi-elemental geochemical characterization of the ore was carried out within ALS Romania, Roșia Montana Geochemistry facility. The concentrations of 49 chemical elements in the ore were measured including Ag, Au, Bi, Cd, Cu, Fe, Mn, Pb, S, Se, Sn, Te, W, and Zn.

The gold grade was measured by fire assay and ICP-AES and the detection limit has a range between 0.005 and 10 ppm. Ag was analyzed by HF-HNO_3-$HClO_4$ digestion with HCl leach, ICP-AES finish and the concentrations interval ranging between 1-1500 ppm. The Cu assay was carried out with four acid digestion and ICP finish, the detection limits ranging from 0.001 to 40 %. These analyses were combined with a four acid and ICP-AES method, and Bi, Cd, Fe, Mn, S, Sn, Zn, Pb, Te, Se, W, etc. were tracked. The detection range for each element mentioned is, *i.e.* Bi, 0.01-10,000 ppm; Cd, 0.02-1,000 ppm; Fe, 0.01-50 %; Mn, 5-100,000 ppm; S, 0.01-10 %; Sn, 0.2-500 ppm; Zn, 2-10,000 ppm; Pb, 0.5-10,000 ppm; Te, 0.05-500 ppm; Se, 1-1,000 ppm; and W, 0.1-10,000 ppm.

Results and Discussions

The geochemical analyses aimed to point out the presence of certain metallic elements and their grade. Significant results were obtained for several metallic elements presented in Table 1 by combining the analytical methods mentioned above. The concentration of two metals presented in Table 1, *i.e.* Bi and Sn, exceeds the upper detection limit of the analytical methods. However, the abundance of Bi (> 1 wt %), and the high grade Sn was certified for the analyzed ore sample.

Table 1. The main chemical components in the ore deposit from Blidar Contact, Băița Bihor ore deposit.

Element		Ag ppm	Au ppm	Bi wt%	Cd ppm	Cu wt%	Fe wt%	Mn wt%	Pb wt%	S wt%	Se ppm	Sn ppm	Te ppm	W ppm	Zn wt%
Content		530	0.91	>1	115	22.8	13.5	0.16	0.29	7.85	110	>500	120.5	530	0.69

The geochemistry results (Table 1) indicate the polymetallic character of the ore. Copper grade is extremely elevated (over 22 wt %) and it is accompanied by less economically attractive Pb and Zn grades. The precious metals are well represented with significant Au and Ag grades, *i.e.* about 1 ppm and 530 ppm respectively. The couple W-Sn has also high grades with over 500 ppm for each element. Te, Se and Cd also show high concentrations that precisely reflect the mineralogy of the ore.

Recent mineralogical results on similar ore samples from Blidar Contact (Andrii and Tămaș, 2015 and 2017) obtained by optical microscopy, SEM-EDS semi-quantitative chemical data and back-scattered electrons images presently allow to correlate at least in part the geochemical results to the mineralogy of the ore. The above-mentioned authors confirmed the copper-rich character of the Blidar Contact ore body with bornite as main Cu-bearing mineral, which shows partial replacement by several secondary Cu-sulfides, *i.e.* digenite, chalcocite and covellite, and is accompanied by chalcopyrite, sphalerite, hessite, electrum, wittichenite, and kesterite.

According to the above mentioned results, the abundance of Cu bearing sulfides, *e.g.* digenite, chalcopyrite, and especially bornite is responsible for high Cu grade and in part (*i.e.* bornite and chalcopyrite) for Fe grade. Wittichenite was identified for the first time in Băița Bihor ore deposit by Giușcă (1941) from the Blidar Contact area, and was confirmed by SEM-EDS data by Andrii and Tămaș (2017). The presence of wittichenite and other related Bi-bearing minerals could explain the high-bismuth grade (over 1 wt %; Table 1).

According to the available mineralogical data, *e.g.* Andrii and Tămaș (2015 and 2017), the main source of silver seems to be hessite. The presence of native gold in the ore from Blidar Contact, reported recently by Andrii and Tămaș (2015) is also confirmed by the Au bulk grade (0.91 ppm, Table 1). Hessite seems to be the most important source of Te as well. However, one cannot exclude the possible occurrence of other Te-bearing minerals, which were previously described from Băita Bihor, *e.g.* cervelleite (Cook and Ciobanu, 2003), tetradymite (Cook et al., 2002), joseite-A (Cioflica and Lupulescu, 1995), and for this reason Băița Bihor is an ore deposit with a dominant Bi(-Te) trace signature (Harris et al., 2013).

The high Se grade could be related to Se-bearing minerals or to minerals that host Se impurities. It is worth to be mentioned that naumannite (Ag_2Se) and clausthalite (PbSe) have been mentioned by Cook et al. (2002) from Băița Bihor ore deposit. Pekoite ($PbCuBi_{11}(S,Se)_{18}$) and friedrichite ($Pb_5Cu_5Bi_7(S,Se)_{18}$) that can incorporate small amounts of Se have been also described from Blidar Contact by Shimizu et al. (1998).

The Zn grade in the analyzed ore (Table 1) is certainly related to sphalerite that was described from similar samples by Andrii and Tămaș (2015 and 2017). Sphalerite can accommodate significant quantities of impurities, *e.g.* Fe, Mn, Cd, etc (Cook et al., 2009). It seems that Mn and Cd from the analyzed ore (Table 1) are related to sphalerite. Another Mn-bearing mineral was recently described from Băița Bihor, *i.e.* grațianite (Ciobanu et al., 2014), but this mineral was not identified so far in the studied samples. The Pb grade (Table 1) is likely linked to the presence of galena within the ore.

The geochemical data (Table 1) indicate high W and Sn grades. The occurrence of kesterite (Andrii and Tămaș, 2017) correlates with the high Sn grade, while W should correlate with a W-bearing mineral. It is worth to mention that scheelite ($CaWO_4$) has been described from Blidar Contact by Superceanu (1956) and seems to be the likely candidate for the significant W grade in the analyzed sample.

Conclusions

The present work brings new geochemical data regarding the so-called Blidar Contact ore body from Băița Bihor. These new data validate the polymetallic character of the ore (Cu, Au, Ag, Bi, Sn, W) and allow to propose some possible correlations among these data and the already published mineralogical data. While for most of the analyzed chemical elements it was possible to tight up a connection mineralogy-geochemistry based on recent mineralogical investigation on similar samples, *i.e.* Cu, Bi, Ag, Te, Sn, etc., for W and Se the connection is inferred based on broader mineralogical data reported earlier (*e.g.* Superceanu, 1956; Shimizu et al., 1998; Cook et al., 2002).

References

Andrii M.P., Tămaș C.G. (2015) Mineralizații cuprifere în zăcământul Băița Bihor, Munții Apuseni - studii mineralogice comparative. In: Bucur I.I. et al. (eds.) - Sesiunea științifică anuală „Ion Popescu Voitești”, Cluj-Napoca, 4 decembrie 2015, p. 1-4

Andrii M.P., Tămaș C.G. (2017) Preliminary Mineralogical Data on Bi- and Sn-minerals from Băița Bihor Ore Deposit, North Apuseni Mountains, Romania. Sesiunea Științifică “I.P. Voitești” 2017, 15 decembrie, 2017, Departamentul de Geologie, Universitatea Babeș-Bolyai, p. 1-8

Berza T., Constantinescu E., Vlad Ș.N. (1998) Upper Cretaceous Magmatic Series and Associated Mineralisation in the Carpathian - Balkan Orogen. Resource geology, vol. 48, no. 4, p. 291–306.

Ciobanu C.L., Brugger J., Cook N.J., Mills S.J., Elliot P., Damian G., Damian F. (2014) Graţianite, $MnBi_2S_4$, a new mineral from the Băiţa Bihor skarn, Romania. American Mineralogist, 99(5-6), p. 1163-1170.

Cioflica G., Vlad Ș., Stoici S. (1971) Repartition de la mineralization dans le skarn de Băița Bihorlui. Revue Romaine de Geol, Geoph.,Geogr., Seie Geologie, 15, p. 43-58.
Cioflica G., Vlad Ș., Iosif V., Panican A. (1974) Metamorfismul termic și metasomatic al formațiunilor paleozoice din unitatea de Arieșeni de la Băița Bihorului. St. cerc. geol., geofiz., geogr., Seria geologie, 19, p. 43-68.
Cioflica G., Vlad Ș., Volanschi E., Stoici S. (1977) Skarnele magneziene cu mineralizațiile asociate de la Băița Bihorului. St. cerc. geol., geofiz., geogr., Geologie, 22, p. 39-57.
Cioflica G., Jude R., Lupulescu M. (1995) Petrometalogenetic models in the areas with the end Maastrcthian-Paleocene granitoid intrusions of Romania. Studia Univ. BabeșBolyai, Geologia (Petrometalogeny) 40/1, Cluj-Napoca, p. 41-54.
Cioflica G., Lupulescu M. (1995) New data on joseite-A from Baita Bihor Mine (Bihor Mountains, Romania). Romanian Journal of Mineralogy 77, Suppl. 1, p. 12-13.
Cook N.J., Ciobanu C.L., Bogdanov K. (2002) Trace mineralogy of the Upper Cretaceous Banatitic Magmatic and Metallogenetic Belt, SE Europe. 11th IAGOD Symp. Geocongress. CD vol. of ext. Abstr, Geol. Surv. Namibia.
Cook N., Ciobanu C. (2003) Cervelleite, Ag_4TeS, from three localities in Romania, substitution of Cu, and the occurrence of the associated phase, Ag_2Cu_2TeS. Neues Jahrbuch für Mineralogie - Monatshefte. 7, p. 321-326.
Cook N.J., Ciobanu C.L., Pring A., Skinner W., Shimizu M., Danyushevsky L., Saini-Eidukat B., Melcher F. (2009) Trace and minor elements in sphalerite: a LA-ICPMS study. Geoch. Cosmoch. Acta, 73, p. 4761-4791.
Gallhofer D., Quadt A., Peytcheva I., Schmid, S., Heinrich C. (2015) Tectonic, magmatic and metallogenic evolution of the Late Cretaceous Arc in the Carpathian - Balkan orogen. Tectonics, 34, 1813–1836.
Giuşcă., D. (1941) Note préliminaire sur la minéralisation des gisements de contact de Băiţa Bihorului. Mem. Sect. Științ. Acad. Roum. ser. II, XVI/6, p. 681-693.
Harris C., Pettke T., Heinrich C.A., Rosu E., Woodland S., Fry B. (2013) Tethyan mantle metasomatism creates subduction geochemical signatures in non-arc Cu–Au–Te mineralizing magmas, Apuseni Mountains (Romania). Earth and Planetary Science Letters, 366, p. 122-136.
Heinrich A., Neubauer F. (2002) Cu – Au – Pb – Zn – Ag metallogeny of the Alpine – Balkan – Carpathian – Dinaride geodynamic province. Mineralium Deposita. 37, p. 6-7.
Ilinca G., Makovicky E., Topa D., Zagler G. (2010) Cuproneyite, $Cu_7Pb_{27}Bi_{25}S_{68}$, a new mineral from Băiţa Bihor, Romania. Canadian Mineralogist, 50, p. 353-370.
Mumme W.G., Žák L. (1985) Paderaite, $Cu_{5.9}Ag_{1.3}Pb_{1.6}Bi_{11.2}S_{22}$, a new mineral of the cuprobismutite-hodrushite group. Neues Jahrb. Mineral. Monatsh', p. 557 -567.
Shimizu M., Kato A., Cioflica G., Lupulescu M., Shimizu M. (1998) Friedrichite from Băița Bihor, Romania. Canadian Mineralogist 36, p. 861-868.
Stoici D.S. (1974) Studiul geologic şi petrografic al bazinului superior al Crişului Negru - Băiţa Bihor cu privire specială asupra mineralizaţiei de bor şi a skarnelor magneziene. Inst. Geol. Geofiz., Stud. tehn. econ., Ser. I, Min.-Petr., 7, 198 p.
Stoici D.S. (1983) Districtul metalogenetic Băiţa Bihorului: cercetări geologice şi miniere. Editura Academiei Republicii Socialiste România, București, 189 p.
Stoicovici E., Selegean I. (1970) Considerațiuni la cunoașterea magmatismului banatitic din Munții Bihorului. Studia Univesitatis Babe-Bolyai, Seria Geologia, vol. 15/2, p. 3-15.
Superceanu C. (1956) Noi apariții de scheelit în zăcămintele de conact din provincia geochimică a banatitelor. Rev. min., p. 4-5.
Udubașa G. (2003) Outstanding mineral occurrences in Romania: what’s new? Acta Mineralogica-Petrographica, Abstract Series 1, 106 p.
Vlad Ș.N. (1993) Geologia resurselor minerale. Curs universitar. Partea I: Zăcăminte metalifere şi nemetalifere. Universitatea Ecologică, București, 90 p.
Vlad Ș.N. (2011) Perspective targeting CuAuMo porphyries of Romanian Carpathians: blind porphyry mineralization and its variable distal expression as vein and skarns. Cent. Eur. J. Geosci, 3(3), p. 318-335.
Vlad Ș.N., Berza T. (2003) Banatitic magmatic and metallogenetic belt: metallogeny of the Romanian Carpathians segment. Studia Universitatis Babes-Bolyai, Geologia, XLVIII, 1, p. 113-122.

Žák L., Fryda J., Mumme W.G., Paar W.H. (1994) Makovickyite, $Ag_{1.5}Bi_{5.5}S_9$ from Băiţa Bihorului, Romania. The 4P natural member of the pavonite series. Neues Jahrb. Mineral., Abh. 168, p. 147-169.

Zimmerman A., Stein H.J., Hanah J.L., Koželj D., Bogdanov K., Berza T. (2008) Tectonic configuration of the Apuseni-Banat-Timok-Srednogorie belt, Balkans-South Carpathians, constrained by high precision RE-OS molybdenite ages. Miner. Deposita, 43, p 1-21.